Silicon Nitride Films Grown by PEALD

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Silicon nitride deposition process using plasma enhanced ALD (PEALD) technique is demonstrated in this work. The effect of deposition temperature, silicon precursor and plasma power on the film growth is studied. Optical properties and atomic concentrations of the film are investigated.

1 Introduction

Silicon nitride (Si_3N_4) is an attractive material for barrier [1], optical and semiconductor [2] applications. This letter presents effects of deposition parameters on the film growth. Optical properties and atomic concentrations are also reported.

2 Theory

Plasma gas is a complicated mixture of electrically charged and neutral species. From the ALD point of view the species can be simplified for three groups 1) neutral molecules such as N_2, 2) radicals such as N^* and 3) ions such as N_2^+. Neutral molecules play usually negligible role. Radicals take active role in the deposition process. Ions are usually avoided because of the high energy which may lead to the sample damages. In direct plasma reactor plasma is ignited very close to the substrate which leads to ionic collisions to the substrate. Remote plasma reactor is a chamber where the plasma discharge is separated from the substrate by 1) distance or 2) grounded ion blocking plate. All ions can't be blocked by the remote plasma as shown by Heil et. al. [3].

3 Experimental Details

Silicon nitride films were deposited using Beneq TFS 200 reactor equipped with hot wall plasma head. The plasma head was capacitively coupled (CCP) with direct and remote plasma options as shown in Fig. 1. High purity nitrogen (99.9999 %) was used as carrier gas and plasma gas. The effect of ammonia (NH_3) on the deposition rate was also tested. Bis(tert-butylamino)silane (BTBAS), tris(dimethylamino)silane (3DMAS) and AP-LTO® 330. were tested as the silicon precursors. 3DMAS and BTBAS were pulsed in to the reactor using load and release method. It means that the precursor container was filled by N_2 gas. After the filling pressure was released into the ALD reactor by opening the

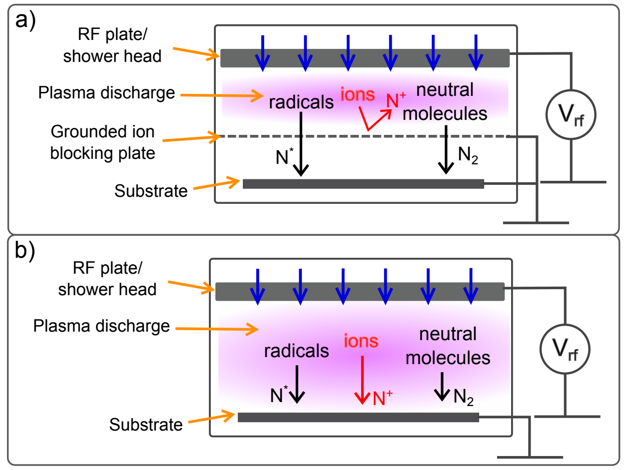

Figure 1: Schematics of the Beneq TFS 200 a) remote b) direct plasma.

pulsing valve. Atomic concentrations were determined using Time-of-Flight Elastic Recoil detection analysis (TOF-ERDA). The optical film properties were investigated using PerkinElmer Lambda 900 spectrophotometer.

4 Results

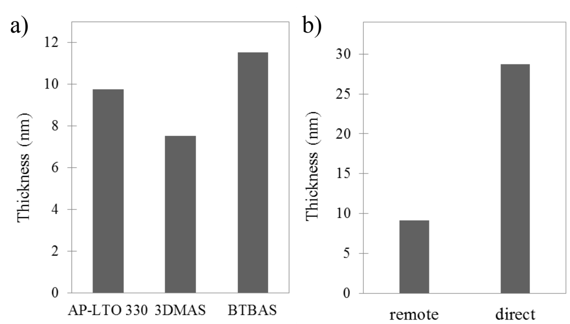

Figure 2: Thickness of the SiN film as the function of a) precursor and b) plasma mode.

When the silicon precursors AP-LTO 330, 3DMAS and BTBAS were compared it was found that BTBAS led

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to thickest deposition which can be seen from Fig. 2 a. The differences are not significant. But a difference was observed when the remote and direct plasma mode were compared. With the same number of cycles (1000) direct plasma was approximately three times faster as one can see from Fig. 2 b.

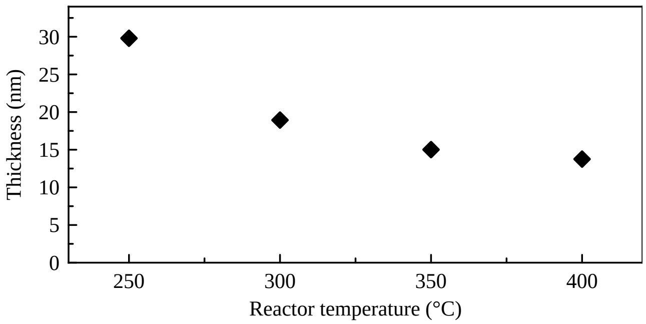

Figure 3: Film thickness as a function of reactor temperature.

When reactor temperature was varied from 250 to 400 °C it came out that the film thickness is decreased when the temperature is increased as shown in Fig. 3. Film started to absorb light when the wavelength was lower than 300 nm. From 300 to 800 nm the refractive index of the film followed the Caughy's equation 1

$$n = 1.911 + \frac{0.000796}{\lambda^4}, \qquad (1)$$

where the unit of the wavelength λ is micrometer.

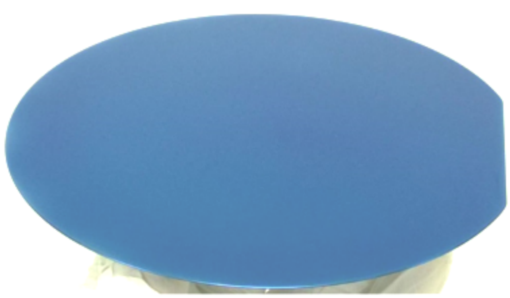

Figure 4: Photo of 150 mm (6 inch) wafer coated with 81 nm thick PEALD Si_3N_4.

The uniformity of the 81 nm thick film shown in Fig 4 was 1.2 % $(1 - \sigma/average)$. As it can be seen the process is scalable but it came out that conformal radical flow was required to achieve good film uniformity. The etch rate of the film grown at 350 °C was investigated by sinking it to 1 % hydrofluoric acid at the room temperature. The etch rate was 0.19 nm/min which is relatively low for Si_3N_4.

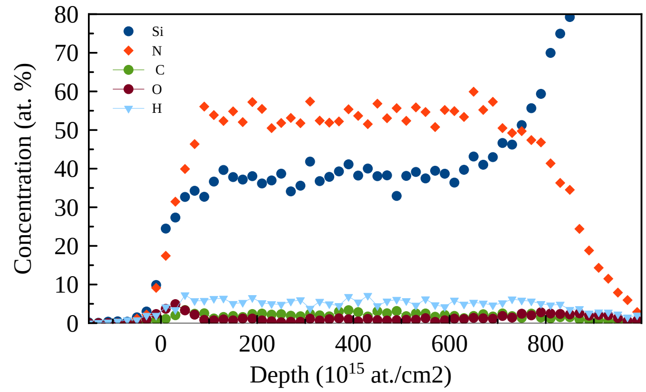

Figure 5: Atomic concentrations depth profiles measured by TOF-ERDA.

Atomic concentrations of the film as the function of the depth are presented in Fig.5. The deposition temperature was 350 °C. It can be seen that there is an oxygen peak near the surface. The oxygen concentration in the bulk film was 0.8 ± 0.1 %. Other impurities originating from the ligand were hydrogen 5.5 ± 0.5 % and carbon 2.2 ± 0.1 %. The N/Si atomic ratio was 1.41 which indicates that the film stoichiometry is close to Si_3N_4. The precursor for this sample was BTBAS.

5 Summary

Silicon nitride films were deposited using Beneq TFS 200 hot wall plasma ALD. Direct plasma led to three times faster deposition rate compared to the remote plasma. No big difference between the silicon precursors was observed. The film was optically transparent when the wavelength was higher than 300 nm.

6 Acknowledgements

The TOF-ERDA of thin films was done at University of Jyväskylä. Further information regarding elemental analysis please contact professor Timo Sajavaara.

References

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